GAS PURIFICATION APPARATUS AND PROCESS

Field of the Invention

[0001] The present invention relates to purification of industrial gases such as carbon dioxide, helium and argon, and especially to removal of hydrocarbon and/or oxygen by catalytically assisted techniques.

Background of the Invention

[0002] Industrial gases are often required to meet purity specifications. In order to meet these specifications, various impurities must be removed from the gases. Catalytic combustion plays a role in the removal of many impurities. The use of a catalyst allows the combustion to proceed at temperatures lower than would otherwise be necessary, although a temperature of as high as 1000 °F may still be required.

[0003] There are numerous examples of catalytic combustion applications in gas purification. It is used to remove hydrocarbon contamination from CO_2. Hydrocarbons removed in this manner include ethane, benzene, methanol, ethanol, and acetaldehyde. Oxygen is added to the CO_2 stream if necessary, and catalytic combustion converts the hydrocarbons into CO_2 and water. The water is easily removed in downstream dryer beds. Oxygen can also be removed from CO_2 by adding hydrogen to the CO_2 stream and passing it over a catalyst to form water. This is employed in point-of-use purifiers where low oxygen levels are required. Hydrogen is removed from helium by this technique because the two gases are difficult to separate by other means such as distillation. Oxygen is added to the helium and catalytic combustion converts the hydrogen to water. The

water and excess oxygen are easily removed from the helium. Catalytic combustion is also used in argon purification. Because oxygen and argon are difficult to separate by distillation, hydrogen is added to the argon stream and combusted with the oxygen over a catalyst to form water. The water is easily removed from the argon.

[0004] Heat management is very important in all the catalytic combustion applications listed above. Temperatures of 500-1000 °F are required for the catalytic combustion of hydrocarbons in CO_2. The process would not be economical if energy had to be expended to heat the CO_2 to these temperatures. Heat must be recovered from the hot gas and transferred to the incoming gas to reduce the amount of energy required to heat it and to make the process cost-effective. Heat is produced during the combustion of contaminants in all catalytic combustion applications. This heat is used to preheat the incoming gas when the combustion takes place at elevated temperatures, but it must be removed from the gas stream in all cases to allow for further downstream processing of the gas.

[0005] Catalytic combustion is a well-known technique for removal of impurities from gases, and many examples of it exist in the prior art. It is normally referred to as catalytic oxidation when hydrocarbons and/or hydrogen are removed from the gas by reaction with oxygen to form CO_2 and water in the case of hydrocarbons and water alone in the case of hydrogen. The combustion process is referred to as "deoxo" when oxygen is removed from the gas by reaction with hydrogen to form water.

[0006] A generic catalytic oxidation system is described in the literature (Kohl and Nielsen, 1997) for use in removing volatile organic compounds from an air

stream. The catalytic oxidation system consists of three unit operations: a heat exchanger, a burner, and a catalyst bed. The air that is to be purified first passes through one side of the heat exchanger where it is heated by indirect contact with hot gas leaving the catalyst bed. The preheated air then flows to the catalyst bed where its temperature is raised further by mixing it with hot combustion gases from the burner. The hot mixture has a temperature high enough to allow oxidation reactions to occur over the catalyst. The hot air flows across the catalyst where the volatile organic compounds react with oxygen to form CO_2 and water, which are not harmful pollutants. Heat is released by this reaction, and the temperature of the air stream increases somewhat. The hot purified air exits the catalyst bed and flows into the heat exchanger where it is cooled by indirect contact with the incoming air.

[0007] The amount of heat that must be added to the air by combusting fuel in the burner is determined by three factors: the amount of combustible contaminants in the air, the efficiency of the heat exchanger, and the amount of heat loss between the unit operations. If the air contains more contaminants, more heat will be generated from their combustion. If enough contaminants are present, no heat will need to be added. Because of inefficiencies in gas-to-gas heat transfer, it is impossible to recover all the heat from the purified air leaving the catalyst bed into the incoming contaminated air. The amount of heat recovery is increased by using a larger and more costly heat exchanger or more than one heat exchanger. Any heat lost between the catalyst bed and the heat exchanger, between the heat exchanger and the heater, and between the heater and the catalyst bed will increase the amount of energy required from the

heater. The cost of heating the air is reduced by minimizing the heat loss.

[0008] The catalyst in the system described by Kohl and Nielsen often consists of a platinum group metal deposited on an alumina support. The support is either in the form of pellets that are arranged in a packed reactor bed or in the form of a monolithic structure whose passages are coated with the catalyst material. Older designs used the pellet catalysts exclusively, but more modern systems often employ monoliths.

[0009] Figure 1 shows one kind of previously known system for CO_2 purification. Hydrocarbons in the impure CO_2 feed 101 are oxidized to CO_2 and water over a catalyst. The catalytic oxidation system again consists of three unit operations: a heat exchanger 102, a heater 103, and a catalyst vessel 104, all of which are distinct units connected by suitable piping. The CO_2 flows through the shell side of a shell and tube heat exchanger 102 for preheating, through a supplemental heater 103 for heating to reaction temperature, through the catalyst vessel 104 for reaction of the hydrocarbons, and through the tube side of the heat exchanger 102 for cooling. The purified CO_2 stream 107 continues on for further processing in the CO_2 plant.

[0010] If the CO_2 contains enough combustible contaminants, its temperature will rise to such a degree that the incoming gas is preheated to too great a temperature. In this case some of the incoming gas is bypassed around the heat exchanger via bypass line 105 controlled by bypass valve 106. The cool bypass gas is mixed with the preheated gas before entering the reactor to establish the correct initial combustion temperature. The supplemental heater 103 is normally an electric

heater. The catalyst comprises a platinum group metal deposited on alumina in pellet form. Operation of a catalytic oxidation unit in a CO_2 plant differs from that of the system described in Kohl and Nielsen in two major ways. Oxygen must be added to the CO_2 so that combustion can take place over the catalyst, while sufficient oxygen is always present during air purification. CO_2 purification takes place at a pressure of approximately 300 psig, while air is processed at atmospheric pressure.

[0011] The use of catalytic oxidation for hydrocarbon removal from CO_2 is described in U.S. Patents 3,317,278 and 4,460,395. In both patents the catalytic oxidation system consists of separate vessels for the heat exchanger, heater, and catalyst vessel.

[0012] Catalytic oxidation has previously been used in helium plants for removal of hydrogen from helium. Hydrogen content of approximately 2% is removed by adding oxygen to the helium and using it to oxidize the hydrogen. The catalytic oxidation arrangement for helium purification is slightly different than that described for CO_2 and air. Hydrogen reacts with oxygen at a much lower temperature than do hydrocarbons, so heat recovery is not an important issue. Heat must be rejected from the purified helium instead so that it can be processed further. The helium stream containing hydrogen and oxygen is preheated slightly to approximately 150 °F. It passes into a catalyst vessel where a portion of the hydrogen reacts with oxygen. Complete oxygen removal is not possible over this catalyst because the temperature rise due to combustion would be too great and the catalyst would be destroyed. The hot partially purified helium stream flows through a heat exchanger where it exchanges heat with a cooling

fluid. It then passes to another catalyst bed where the remainder of the hydrogen reacts. Later processing steps cool the helium further and remove the water formed during hydrogen oxidation. The catalytic oxidation portion of the helium plant consists of five separate vessels: a heater, two catalyst vessels, and two heat exchangers. The catalyst consists of pellets of a platinum group metal deposited on alumina.

[0013] Catalytic combustion has also been used in the removal of oxygen from argon. It is referred to as "deoxo" in this case. Liquid argon from the crude argon column containing approximately 1.5% oxygen is vaporized and hydrogen is added to the gas stream. The mixture is compressed and passed to a catalyst bed where the hydrogen and oxygen react. The gas is heated by this reaction and it is cooled in a heat exchanger downstream of the reactor. The water formed in the reaction is removed from the argon stream downstream of this heat exchanger. The deoxo system consists of two separate vessels: the catalyst vessel and the heat exchanger. The catalyst consists of alumina pellets with a platinum group metal deposited on them.

[0014] The use of a deoxo unit for removal of oxygen from argon is described many places in the literature. An article by Latimer (February 1967) is one example. U.S. Patent 6,168,774 describes a compact deoxo system for removal of oxygen from nitrogen at a small scale.

[0015] Because the cost of heating the inlet gas for a catalytic combustion system can be so expensive, heat integration of these systems has been reported in the literature. Eigenberger and Nieken (January 1994) discuss the advantages to be gained by better integration

of the catalyst bed with the heat recovery mechanisms. They concentrate on regenerative heat recovery for the most part. Regenerative heat recovery involves direct contact of the fluids being cooled and heated with a large thermal mass. One example of regenerative heat recovery is the flow of hot gas over refractory material to heat it. The gas flow path is then switched and cool gas flows over the hot refractory material and is heated by it. This invention is not concerned with regenerative heat recovery. Recuperative heat recovery involves the indirect contact of two fluids in a heat exchanger, and this invention does concern recuperative heat recovery. When Eigenberger and Nieken do consider recuperative heat recovery, they propose filling the tubes of the heat recovery heat exchanger with catalyst. While effective for heat recovery, this method is likely to add additional expense to the system. The present invention is not concerned with loading catalyst into the tubes of a shell and tube heat exchanger.

[0016] U.S. Patent 5,914,091 proposes a point-of-use catalytic oxidation unit for volatile organic compound removal. This compact unit is designed to sit in a small well-insulated cabinet to minimize heat loss. The heat exchanger and the catalyst vessel are in close proximity, but they are separate vessels. The differentiation of vessels is not as important in this application as in those at higher pressures because this application is for gas at essentially atmospheric pressure.

[0017] However, there has remained a need for a system that provides the combination of features and freedom from drawbacks that the present invention provides.

Brief Summary of the Invention

[0018] One aspect of the present invention is apparatus useful for purifying a gas stream, comprising

(a) a shell-and-tube heat exchanger comprising a shell inlet and a shell outlet in fluid communication with the shell inlet, and further comprising a plurality of tubes each having an inlet and an outlet;

(b) a catalyst system comprising a catalyst supported on a monolithic unitary support having passages therethrough, the support having a length and upstream and downstream ends at opposite ends of the length, wherein the diameter of said support is from one-half to two times the diameter of the shell of the heat exchanger, and wherein the downstream end of said support is connected in fluid communication with the inlets of said tubes by a passageway whose length does not exceed the length of the support and whose diameter is at no point less than the smaller of the diameter of said support and the diameter of said shell; and

(c) a source of gas to be purified in fluid communication with said upstream end of said support.

[0019] Another aspect of the present invention is a method for purifying a gas stream, comprising passing the gas through said apparatus under conditions effective to remove one or more contaminants from said gas stream.

[0020] As used herein, a "shell-and-tube heat exchanger" is a heat exchanger comprising a plurality of tubes aligned generally parallel to each other and whose outer surfaces are spaces apart from each other, a pair of plates (often termed "tube sheets") through which the

tubes pass and to which the outer surfaces of the tubes are sealed at or near each end of the tubes, and a shell surrounding all of the tubes and sealed to the outer edges of the tube sheets thereby defining an enclosed space which contains all of the tubes. The shell also extends past the tube sheet at both ends of the heat exchanger and each end normally terminates in a flange connection. The volume between the flange connection and the tube sheet is termed a "heat exchanger bonnet".

[0021] As used herein, the "diameter" of the support, of the shell, and of the passageway is, if the cross-section of the object is circular, the diameter of the circle, and if the cross-section is not circular, the length of the longest line segment that can be drawn between two points on the edge of the cross-section passing through the center of the cross-section.

[0022] As used herein, the "length" of the passageway is the sum of the distances between the downstream end of the support and the inlets of each tube, divided by the number of such tubes.

Brief Description of the Drawings

[0023] Figure 1 is a flowsheet of a known system for purification of a carbon dioxide stream.

[0024] Figure 2 is a flowsheet of a carbon dioxide purification system according to the invention.

[0025] Figure 3 is a longitudinal cross-sectional view of a portion of the system of Figure 2.

[0026] Figure 4 is a flowsheet of an argon purification system according to the invention.

[0027] Figure 5 is a flowsheet of a helium purification system according to the invention.

[0028] Figure 6 is a flowsheet of another helium purification system according to the invention.

[0029] Figure 7 is a flowsheet of another carbon dioxide purification system according to the invention.

[0030] Figure 8 is a longitudinal cross-sectional view of a portion of the system of Figure 7.

Detailed Description of the Invention

[0031] The present invention allows a catalytic combustion system to be constructed for a lower capital cost. It also reduces the heat leak from the system; this will reduce operating costs in cases where heat input to the system is required. All the prior art for pressurized catalytic combustion processes using recuperative heat exchange shows systems with separate catalyst vessels and heat exchangers. This invention uses the properties of unitary, monolithic (one-piece) catalyst supports to couple the catalyst directly to the heat exchanger. The catalyst is installed in a spool piece that is attached by a flange connection to the bonnet of the heat exchanger. The cost of the heat exchanger remains unchanged, but the spool piece costs significantly less than a separate catalyst vessel. This is especially advantageous for pressurized systems because it reduces the number of pressure vessels that must be coded and pressure protected. Applications that use two catalyst beds on opposite ends of a heat exchanger benefit even more from the invention. In these cases, spool pieces containing catalyst are attached to both ends of the heat exchanger, and the number of

pressure vessels is reduced from three to one. Use of the monolithic catalyst also allows the catalytic combustion system to be positioned in any orientation to better integrate the system into the overall plant. Pellet-based catalytic combustion systems must have the catalyst vessel oriented in a vertical position. The close coupling of the catalyst and the heat exchanger allows less heat to escape from the system than does piping between a catalyst vessel and the heat exchanger. Reduced heat loss means that less heat must be added to the system in order for it to reach reaction temperature in cases where addition of heat is required. Operating costs will be reduced as a result.

[0032] Preferably, the heat exchanger is cylindrical. It is also preferred that the monolithic catalyst support is cylindrical and is situated in a cylindrical casing (or "spool piece") at least as long as, and more preferably longer than, the catalyst support. The inlets of the tubes of the heat exchanger closest to the catalyst support, and the end of the catalyst support closest to that inlet, are spaced apart by a distance of no more than the length of the support. The heat exchanger shell and the cylindrical casing are preferably of the same diameter but where the diameters differ the connection can be made by an appropriately shaped sheet. The outside diameter of the catalyst support is slightly (approximately 0.1 inches - 0.5 inches) less than the inside diameter of the cylindrical casing so that the support can be positioned inside the casing.

[0033] Typical dimensions are a diameter of 1 to 36 inches each for the heat exchanger and the catalyst support, and a length of 3 to 84 inches for the catalyst

support. The passageway, also known as the free space, between the adjacent ends of the catalyst support and of the tube inlets of the heat exchanger, typically has a length of 3 to 18 inches.

[0034] The invention will be described in more detail in the following illustrative embodiments.

[0035] **CO_2 purification in a production plant.** A catalytic oxidation system for the purification of CO_2 is shown in Figure 2. CO_2 stream 10 at a pressure of 280-340 psig and a temperature of approximately 150-200 °F enters the shell side of shell and tube heat exchanger 11. CO_2 stream 10 contains enough oxygen to oxidize the contaminants that will react over the catalyst. The oxygen in the CO_2 stream 10 may be native from the source or it may have been injected specifically for the catalytic oxidation. An excess oxygen monitor is positioned downstream of the reactor, normally after the gas is cooled. The signal from this monitor is used to control the injection of oxygen in the form of liquid oxygen, VPSA oxygen, or air upstream of stream 10. The control system normally maintains the oxygen level downstream of the reactor at 500 to 2500 ppm. This level may be higher if significant oxygen is present in the CO_2 source gas. Composition of the CO_2 stream at various locations in the process is shown in Table 1. The CO_2 is heated via heat exchange with hot gas flowing counter-currently through the tubes of the heat exchanger. The CO_2 exits the shell side of the heat exchanger at a temperature of 450-950 °F through pipe 12. It passes through electric heater 13 and its temperature is raised to 550-1050 °F. (The temperature required for the reaction depends upon the identity and quantity of the

contaminants that must be removed.) The CO_2 then flows through pipe 15 into the catalyst spool piece 19.

[0036] The catalyst spool piece is shown in more detail in Figure 3. The spool piece contains the monolith catalyst 18 and is directly attached to the bonnet of heat exchanger 11 by a flange connection. In this and all other embodiments of the invention, an optional gas distributor 16 may be positioned upstream of, and near the entrance of, the spool piece to ensure that the gas is distributed equally to all the catalyst passages. This optional distributor may consist of a perforated plate or some other dispersion device. The contaminants in the CO_2 that can be oxidized react with oxygen as they pass through the monolith catalyst. The catalyst consists of a platinum group metal deposited on a monolith substrate. The monolith is in the form of a ceramic honeycomb, a ceramic foam, or a metal foil. The CO_2 leaves the catalyst spool piece at a temperature of 550-1050 °F. The temperature rise across the catalyst depends on how many contaminants are present in the stream and how many of the contaminants are oxidized over the catalyst.

[0037] Referring again to Figure 2, after exiting from the catalyst support the CO_2 stream 17 flows through the remainder of the spool piece 19 into the tube side of shell and tube heat exchanger 11. It flows counter-currently to the inlet stream 10. The heat exchange serves to heat stream 10 and cool the hot gas leaving the catalyst spool piece. The purified CO_2 leaves the heat exchanger as stream 20. It has a temperature of 250-300 °F at this point, and it continues on for processing in the CO_2 production plant. This processing includes chilling, water removal, drying with an adsorbent, liquefaction, and stripping of light contaminants.

[0038] If the contaminant level in the CO_2 stream is high enough, the temperature of stream 17 may rise to the point where too much heat is transferred to stream 12 and the reactor inlet temperature starts to rise. If this situation arises, some of inlet stream 10 is bypassed around heat exchanger 11 through bypass control valve 14. The amount of gas flow through the bypass is adjusted in order to obtain the proper inlet temperature to the reactor. Gas continues to flow through the heater when the bypass valve is opened, but no power is supplied to the heater. This system is not restricted to operation in a vertical arrangement as shown in Figure 2.

[0039] **Argon purification.** A deoxo system for argon purification is shown in Figure 4. Argon containing approximately 1.5% oxygen is vaporized and enough hydrogen is added to the stream to react with all the oxygen present. Composition of the argon stream at various locations in the process is shown in Table 2. The mixture is compressed to 40-75 psig and it has a temperature of approximately 70 °F. This compressed mixture of argon, oxygen, and hydrogen is shown as stream 30. Stream 30 passes into catalyst spool piece 32 and flows through monolith catalyst 33. A detailed view of the spool piece is not shown, but it would look identical to the drawing for CO_2 purification shown in Figure 3. A gas distributor 31 may be positioned near the entrance of the spool piece to ensure that the gas is distributed equally to all the catalyst passages. This optional distributor may consist of a perforated plate or some other dispersion device. The catalyst consists of a platinum group metal deposited on a monolith substrate. The monolith is in the form of a ceramic honeycomb, a ceramic foam, or a metal foil. The oxygen and hydrogen in the argon react over the catalyst. The argon stream

is heated by this reaction. The hot purified argon stream 35 exits the catalyst spool piece and enters the tube side of shell and tube heat exchanger 34. Spool piece 32 and heat exchanger 34 are directly attached to each other by a flange connection. The argon stream is cooled by heat exchange with water or another cooling fluid that flows counter-currently through the shell side of the heat exchanger. The cooled argon stream leaves the heat exchanger at a temperature of 100-200 °F with its oxygen content reduced to a few ppm as stream 36. Stream 36 is processed further in the argon production plant. Cooling water or another cooling fluid enters heat exchanger 34 as stream 37. It is heated as it removes heat from the hot argon stream, and it exits the heat exchanger as stream 38. The system is not limited to the horizontal arrangement shown in the figure.

[0040] **Helium purification.** A catalytic oxidation system for helium purification is shown in Figure 5. Helium is taken from a pipeline at a pressure of 400-600 psig. It can contain as much as 4-5% hydrogen and 3% methane at this point. The helium is preheated slightly in a heater (not shown) to approximately 150 °F. This high pressure helium stream is stream 40. Oxygen is added to stream 40 via stream 39. The amount of oxygen that is added is chosen so that reaction of all the oxygen with hydrogen will not generate heat that raises the temperature of the gas stream above approximately 750 °F; at this temperature undesirable combustion of methane in the stream may begin. Composition of the helium stream at various locations in the process is shown in Table 3. The mixture of helium, hydrogen, methane, and oxygen passes into catalyst spool piece 42 and flows through monolith catalyst 43. A detailed view of the spool piece is not shown, but it would look identical to

the drawing for CO_2 purification shown in Figure 3. A gas distributor 41 may be positioned near the entrance of the spool piece to ensure that the gas is distributed equally to all the catalyst passages. This optional distributor may consist of a perforated plate or some other dispersion device. The catalyst consists of a platinum group metal deposited on a monolith substrate. The monolith is in the form of a ceramic honeycomb, a ceramic foam, or a metal foil. The oxygen and hydrogen in the helium react over the catalyst. The helium stream is heated by this reaction. The hot partially purified helium stream 44 exits catalyst spool piece 42 and enters the tube side of shell and tube heat exchanger 45. Spool piece 42 and heat exchanger 45 are directly attached to each other by a flange connection. The helium stream is cooled by heat exchange with water or another cooling fluid that flows counter-currently through the shell side of the heat exchanger. The cooled partially purified helium stream 46 leaves the heat exchanger at a temperature of 100-200 °F and enters catalyst spool piece 47. A detailed view of spool piece 47 is not shown, but it would look identical to the drawing for point-of-use CO_2 purification shown in Figure 8. Spool piece 47 and heat exchanger 45 are directly attached to each other by a flange connection. Additional oxygen in stream 55 is added to the helium stream via inlet port 56. The inlet port is designed to distribute the oxygen throughout the cross-section of the spool piece. A cross-shaped injector with a graduated series of holes extending from the center of the spool piece on each arm and designed for a constant pressure drop across each hole is one example of an appropriate inlet port. This injector would inject oxygen against the flow direction of the helium stream. Other injector designs can be implemented

as long as they disperse the oxygen sufficiently. Enough oxygen is added to react with the remainder of the hydrogen in the helium stream. The gas stream passes through a gas distributor 49 to ensure that the gas is distributed equally to all the catalyst passages. This distributor may consist of a perforated plate or some other dispersion device. The helium stream then flows through a monolith catalyst 48, where the remainder of the hydrogen and oxygen react. The catalyst consists of a platinum group metal deposited on a monolith substrate. The monolith is in the form of a ceramic honeycomb, a ceramic foam, or a metal foil. The hydrogen content of the helium is reduced to a few ppb. The helium leaves spool piece 47 as stream 50, and it is processed further in the helium production plant. Cooling water or another cooling fluid enters heat exchanger 45 as stream 52. It is heated as it removes heat from the hot argon stream, and it exits the heat exchanger as stream 53. Helium stream 50 must be cooled before it can be processed further in the helium plant.

[0041] The system shown in Figure 5 envisions a separate heat exchanger to accomplish this cooling, but a different embodiment of the invention is shown in Figure 6. Here a second shell and tube heat exchanger 59 is attached via a flange connection to spool piece 47. The helium stream flows through the tubes of this heat exchanger and is cooled by heat exchange with a cooling fluid that flows through the shell side of the exchanger. Neither system is limited to the horizontal arrangement shown in the figures.

[0042] **Point-of-use CO2 purification.** Figure 7 shows a catalytic oxidation system that removes hydrocarbons from CO_2 and then removes excess oxygen remaining from the oxidation. This system is useful for

customers that require low levels of both hydrocarbons and oxygen in their CO_2. The system is designed for installation at the customer site. CO_2 is taken from a product tank of liquid CO_2 and vaporized. Other purification operations can be performed prior to catalytic oxidation. Because the CO_2 is ingredient grade product, hydrocarbon levels are low even before the catalytic oxidation unit. Oxygen is added to the CO_2 at a level of 10-100 ppm. This CO_2 vapor stream is stream 60. Composition of the CO_2 stream at various locations in the process is shown in Table 4. Stream 60 at a pressure of 250-310 psig and a temperature of approximately 60-100 °F enters the shell side of shell and tube heat exchanger 61. The CO_2 is heated via heat exchange with hot gas flowing counter-currently through the tubes of the heat exchanger. The CO_2 exits the shell side of the heat exchanger as stream 62 at a temperature of 450-950 °F. It passes through electric heater 63 and its temperature is raised to 550-1050 °F. (The temperature required for the reaction depends upon the contaminants that must be removed.) Heated CO_2 stream 64 then flows into the catalyst spool piece 65. The spool piece contains the monolith catalyst 67 and is directly attached to the bonnet of heat exchanger 61 by a flange connection. A gas distributor 66 may be positioned near the entrance of the spool piece to ensure that the gas is distributed equally to all the catalyst passages. This optional distributor may consist of a perforated plate or some other dispersion device. The contaminants in the CO_2 that can be oxidized react with oxygen as they pass over the monolith catalyst. The catalyst consists of a platinum group metal deposited on a monolith substrate. The monolith is in the form of a ceramic honeycomb, a ceramic foam, or a metal foil. The CO_2 leaves the catalyst spool

piece at a temperature of close to its inlet temperature. There is little if any heat rise because of the low contamination level of the CO_2. After exiting from the spool piece, purified CO_2 stream 68 flows into the tube side of shell and tube heat exchanger 61. It flows counter-currently to the inlet stream 60. The heat exchange serves to heat stream 60 and cool the hot gas leaving the catalyst spool piece. The purified and cooled CO_2 stream 69 leaves the tube side of the heat exchanger and flows into catalyst spool piece 70. A detailed view of spool piece 70 is shown in Figure 8. CO_2 stream 69 has a temperature of 150-250 °F at this point and it contains a slight excess amount of oxygen (10-50 ppm) that was needed to promote combustion of the hydrocarbons. The amount of oxygen in the CO_2 is measured with an oxygen analyzer and a stoichiometric amount of hydrogen to react with it is added through inlet port 71. The inlet port is designed to distribute the oxygen throughout the cross-section of the spool piece. A cross-shaped injector with a graduated series of holes extending from the center of the spool piece on each arm and designed for a constant pressure drop across each hole is one example of an appropriate inlet port. This injector would inject oxygen against the flow direction of the CO_2 stream. Other injector designs can be implemented as long as they disperse the oxygen sufficiently. The gas flows through gas distributor 73 to ensure that the gas is distributed equally to all the catalyst passages. This distributor may consist of a perforated plate or some other dispersion device. The CO_2 stream then flows through the monolith catalyst 75. The catalyst consists of a platinum group metal deposited on a monolith substrate. The monolith is in the form of a ceramic honeycomb, a ceramic foam, or a metal foil. The

hydrogen and oxygen react over the catalyst and the CO_2 stream is purified of oxygen to a level of less than 0.1 ppm. The CO_2 exits the catalyst spool piece as stream 79 and continues to further processing or to the customer. This system is not restricted to operation in a horizontal arrangement as shown in the figure.

[0043] Any catalyst can be employed so long as it promotes the reaction of oxygen with hydrocarbons, or of oxygen with hydrogen, as the case may be. A natural gas-fired heater or other heat source can be used in place of an electric heater. Other methods of coupling the catalyst support and the heat exchanger that do not involve flanges can also be used and are considered to be within the scope of this invention. One example of an alternative coupling is to position the tube sheet some distance from the end of the heat exchanger shell and to mount the catalyst support within the portion of the shell not occupied by tubes; the housing of the catalyst support would then be the shell itself and not a spool piece attached directly to the shell.

Table 1. Typical stream composition during CO_2 purification.		
	Impure CO_2 (Stream 10)	Purified CO_2 (Stream 20)
CO_2	~99%	~99%
H_2O	~6000 ppm	~9000 ppm
O_2	~3500 ppm	~1000 ppm
CH_4	~1000 ppm	~500 ppm
Other Hydrocarbons	~500 ppm	<3 ppm
BTEX (Benzene, Toluene, Ethylbenzene, Xylenes)	~3 ppm	<10 ppb

Table 2. Typical stream composition during argon purification.

	Impure Argon (Stream 30)	Purified Argon (Stream 36)
Argon	~95%	~99%
H_2	~3%	<0.5%
O_2	~1.5%	<5 ppm

Table 3. Typical stream composition during helium purification.

	Impure Helium (Stream 40)	Partially-Purified Helium (Stream 44)	Purified Helium (Stream 50)
Helium	~70%	~71%	~72%
H_2	~4%	~1.5%	<5 ppb
N_2	~23%	~23%	~23%
CH_4	~3%	~3%	~3%
H_2O	N/A	~1%	~2%
O_2	N/A	~0%	<0.5%

Table 4. Typical stream composition during point-of-use CO_2 purification.

	Ingredient Grade CO_2 (Stream 60)	Partially-Purified CO_2 (Stream 68)	Purified CO_2 (Stream 79)
CO_2	~99.5%	~99.5%	~99.5%
H_2O	<10 ppm	<60 ppm	<60 ppm
O_2	10 - 100 ppm	10 - 50 ppm	<0.1 ppm
H_2	N/A	N/A	<10 ppm
Hydrocarbons	2 - 15 ppm	<0.5 ppm	<0.5 ppm
BTEX (Benzene, Toluene, Ethylbenzene, Xylenes)	<100 ppb	<5 ppb	<5 ppb